

BIOGEOCHEMICAL CYCLES OF CARBON AND SULFUR ON EARLY EARTH (AND ON MARS?)

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Introduction: The physical and chemical interactions between the atmosphere, hydrosphere, geosphere and biosphere can be examined for elements such as carbon (C) and sulfur (S) that have played central roles for both life and the environment. The compounds of C are highly important, not only as organic matter, but also as atmospheric greenhouse gases, pH buffers in seawater, oxidation-reduction buffers virtually everywhere, and key magmatic constituents affecting plutonism and volcanism. S assumes important roles as an oxidation-reduction partner with C and Fe in biological systems, as a key constituent in magmas and volcanic gases, and as a major influence upon pH in certain environments. These multiple roles of C and S interact across a network of elemental reservoirs interconnected by physical, chemical and biological processes. These networks are termed *biogeochemical C and S cycles*.

Cycle Architecture: The overall C and S cycles actually include multiple, nested cyclic pathways (subcycles) that differ with respect to some of their constituent reservoirs and processes [1]. The subcycles also differ with respect to the time typically required for C or S to traverse the subcycle. For example, the "Habitable Subcycle" (HAB) is dominated by biosphere processes and includes C and S reservoirs on the land surface, oceans and atmosphere. Reservoirs in the HAB subcycle exchange rapidly on timescales of hours to 10^3 yr. The "Sedimentary Subcycle" (SED) includes crustal sediments, and these are recycled typically on 10^5 to 10^8 yr timescales. The "Mantle Subcycle" (MAN) includes mantle reservoirs and processes that cycle them with surface and crustal reservoirs on 10^7 to 10^9 yr timescales. The HAB, SED and MAN subcycles all include the C and S hydrosphere and atmosphere reservoirs, which thus unite the entire C and S cycles and allow even their most remote components ultimately to affect the environment and biosphere.

Earth's very dynamic biosphere and climate cycle C and S very rapidly within the HAB subcycle. The pace of the SED subcycle reflects the effects of crustal tectonics on mountain building, basin subsidence, and other factors that affect the crustal C and S reservoirs. The turnover of the MAN subcycle reflects the effects of heat flow and tectonics upon the exchange of C and S between the mantle, surface environment and crust.

Long-Term Change of Earth's Biogeochemical Cycles: The evolution of Earth's mantle and crust

between 4 and 2 billion years ago (Ga) substantially affected the C and S cycles. Following the inevitable decay of radioactive nuclides in the mantle, the heat flow from Earth's interior declined. This decline decreased the rates of both sea floor hydrothermal circulation and the volcanic outgassing of reduced C and S species. The tectonic reworking of Archean continental crust created larger, stabilized continental crust (cratons). Extensive stable shallow-water platforms became sites for productive benthic microbial communities and also for the deposition and long-term preservation of carbonates, organic C, evaporates and sedimentary sulfides. The patterns of carbonate deposition and the abundances of gypsum/anhydrite in associated evaporites indicate that, since 2.5 Ga, seawater concentrations of HCO_3^- and CO_3^{2-} declined and SO_4^{2-} increased. The abundance, style and biological control of mineral precipitation in the global oceans had changed. Biota ultimately came to dominate carbonate precipitation.

(Bio?)geochemical Cycles and Long-Term Changes on Mars: The processes that have driven the geochemical cycles of C and S on Earth probably also operated on Mars, with the potential exception of biological activity. The major differences in the outcomes of geochemical cycling on the two planets arose from substantial differences in the rates of these shared processes. Heat flow declined much faster on Mars, thus its MAN subcycle has operated very slowly for billions of years. This has had negative consequences for atmospheric greenhouse warming. Due to Mars' much weaker tectonics, the martian SED cycle has been dominated instead by the effects of impacts, volcanic and aeolian processes. The absence of a modern ocean and surface-dwelling biosphere has limited the martian equivalent of Earth's "HAB" cycle mostly to abiotic processes that exchange of C and S between the atmosphere and crust. Processes of atmospheric escape of C might have been important on Mars and relatively negligible on Earth.

In the past, did the martian C and S cycles resemble those of Earth more strongly? Has the smaller size of Mars always imposed key differences from Earth? Recent and planned orbital and surface missions are addressing these questions.

Reference: [1] Des Marais D. J. (2001) *Reviews in Mineralogy*, Vol. 43, 555.